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REPORT No. 4/R/68

The Alkaline Hydrolysis of Nitrate Esters

R.T.M. Fraser

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The Alkaline Hydrolysis of Nitrate Esters

by

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22nd May 1968

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CONTENTS

	<u>Page No.</u>
1. Summary	1
2. Introduction	1
3. Experimental	1
3.1 Preparation of Esters	1
3.2 Kinetic Studies	1
4. Discussion	2
4.1 Historical	2
4.2 Specific Rates	3
4.3 Steric Effects	7
4.4 Added Salts	7
5. References	8
Glossary	9
Tables 1 - 5	10 - 17
Key to Figures	18
Figures 1 and 2	

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1. SUMMARY

The stability of nitrate esters in 90% (v/v) ethanol containing sodium hydroxide has been studied. Initial rates of decomposition have been determined at either 30° or 60°C of methyl, n-propyl, n-butyl, n-heptyl, iso-butyl and ethylene glycol mono-nitrates; ethylene glycol, propane 1,3-diol, butane 1,4-diol, pentane 1,5-diol, butane 1,3-diol, butane 2,3-diol, propane 1,2-diol, diethyleneglycol and triethylene glycol dinitrates; glycerol 1- and 2-mono-, 1,3-di- and trinitrate; metriol and NIBG trinitrates; and PETN and 2-nitroethyl nitrate. Alkyl substituents, with retarding inductive effects, stabilize the esters, whereas nitro, nitrate, and hydroxyl groups (with electron attracting properties) increase the rate of hydrolysis by increasing the ionization of α -hydrogens. The effects fall off rapidly as the distance between groups increases. Steric effects are more difficult to assess, but increasing the substitution of the β -carbon appears to decrease the rate of hydrolysis: specific rates range from 4.4×10^{-5} to $1.6 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ (ethyl to iso-butyl nitrate) and from 1.28 to $3.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (NIBG trinitrate to PETN). Ammonium salts decrease reaction rates by combining with hydroxyl ions.

2. INTRODUCTION

Although several investigations have been made (1,2,3) of nitrate ester hydrolysis in alkali solution, only one systematic study (4,5,6) has appeared in the literature. Since even the latter is limited in scope, it was decided to commence a further kinetic study, particularly of those nitrates important in propellant technology.

3. EXPERIMENTAL

3.1 Preparation of Esters

Samples of a number of nitrates were already to hand. Others were prepared by nitration of the parent alcohols by mixed acid. 2-Nitroethyl nitrate was obtained by adding 1 g nitroethanol dropwise to 12.4 g redistilled nitric acid kept at 60°C. After thirty minutes the mixture was poured onto 20 g ice and extracted three times with 5 ml dichloromethane. The extract was dried with sodium sulphate and on evaporation yielded 2-nitroethyl nitrate as a pale yellow oil.

3.2 Kinetic Studies

3.2.1 Slow Rate Reactions

A reaction cell similar to that described previously (4) was constructed from Teflon and mild steel (Figure 1) and used in some of the measurements. Experiments showed, however, that short lengths of polythene tubing heat-sealed at both ends were just as satisfactory as reaction vessels, and the latter were used throughout the study of the slowest reactions.

Alcoholic solutions containing 90% (v/v) ethanol were prepared by weighing and mixing varying amounts of water, absolute ethanol, N sodium hydroxide solution and the ester. Approximately 6 ml of the solution was pipetted into each polythene tube. Care was taken to see that the flame used to seal the open ends of the tubes did not warm the reaction mixture. The filled reaction vessels were placed in a water bath ($60^\circ \pm 0.05^\circ\text{C}$ or $30^\circ \pm 0.1^\circ\text{C}$) and allowed to reach temperature equilibrium before the zero time concentration of hydroxide was determined. Tubes were removed at various time intervals, chilled, opened, and 2 ml aliquots removed for titration with N/50 sulphuric acid, using phenol red as the indicator. Nitrite concentrations were determined by the Griess-Ilosvay method. Results are shown in Table 1.

3.2.2 Moderate Rate Reactions

Faster reactions ($50 < 10^5 k < 400 \text{ M}^{-1} \text{ s}^{-1}$) were run in borosilicate flasks, the solution of sodium hydroxide and that of the ester being allowed separately to reach temperature equilibrium before mixing. Aliquots were removed and titrated as before. Results are shown in Table 2.

3.2.3 Fast Rate Reactions

Reactions with rate constants above $1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ were followed spectrophotometrically at 320 or 340 nm. Both the nitrate esters and their decomposition products exhibit strong absorptions in the ultraviolet region, so that pseudo first order studies could be made, with $[\text{NaOH}] > 10$ [ester], even when the hydroxide ion concentration was less than 0.010 M. Results are shown in Table 3.

3.2.4 Effect of Added Salts

The effect of four salts on the hydrolysis rate of *n*-butyl nitrate at 60°C was measured. Sodium nitrate, sodium perchlorate, ammonium nitrate, and ammonium perchlorate were added in equal concentration to the sodium hydroxide. The results are shown in Figure 2.

4. DISCUSSION

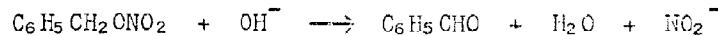
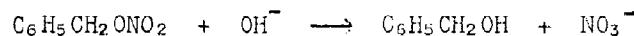
4.1 Historical

The results of early investigations have been summarized by Baker (4): the rate of decomposition is some five hundred times faster in alkali than in acid, and the hydrolysis of polynitrates (such as NG) is complex, with carbonyl compounds, organic acids, and nitrite ion among the products. Hammett (1) studied the reactions of benzyl and *tert*-butyl nitrates in aqueous dioxan, and found that benzaldehyde and isobutene form simultaneously with the corresponding alcohols:

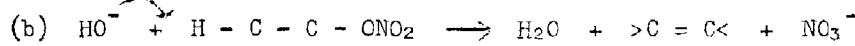


/and

and



Baker (4) considered that the decomposition of the nitrates involved three reactions: (a) nucleophilic substitution to give the parent alcohol and nitrate ion; (b) β -hydrogen elimination to give an olefin and nitrate; and (c) α -hydrogen elimination leading to a carbonyl compound and nitrite ion.



The amount of nitrite formed increases from methyl to ethyl to iso-propyl, and that of olefin from ethyl to iso-propyl to tert-butyl. Reactions are second order (first order in both hydroxyl ion and ester) except in the hydrolysis of tert-butyl nitrate, which is first order - independent of the hydroxyl ion concentration. In general, rates are much slower than for the corresponding hydrolyses of organic bromides (7), and the amounts of olefin formed much less.

It has been pointed out (2) that a further path exists for reaction by nucleophilic substitution, involving fission of the nitrogen-oxygen bond of the nitrate group (d):



Experiments using ^{18}O -labelled water have shown (3) that alkyl-oxygen fission occurs exclusively in tert-butyl nitrate, whereas nitrogen-oxygen fission accounts for 33% of the reaction in n-butyl nitrate and 18% in n-octyl nitrate. The hydrolysis of optically active 2-octyl nitrate yields (2) a mixture of 2-octanol and ethyl 2-octyl ether where two-thirds of the products results from displacement of the nitrogen-oxygen bond. Apparently nitrate esters are borderline cases, with reasonably comparable abilities to undergo both alkyl-oxygen fission like sulphonates (8) and nitrogen-oxygen fission analogous to carboxylic esters (9). Experiments investigating the rate of attack of alkyloxide and aryloxide ions on benzyl nitrate in dry ethanol have been described (6).

4.2 Specific Rates

The measure of stability of a nitrate ester in alkaline solution is the initial specific rate of hydrolysis, k_1 . Subsequent decompositions undergone by any of the reaction products are important in determining both the rate of

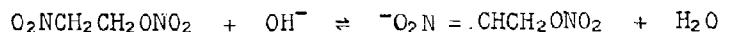
/hydroxyl

hydroxyl ion consumption and the nature of the final products, but they have no bearing on the intrinsic stability of the parent ester. Experimentally three types of kinetic behaviour are found: (a) the specific rate remains constant, within experimental error, throughout the reaction (*m*-ethyl nitrate, *n*-heptyl nitrate, EGDN); (b) the specific rate increases as the reaction proceeds, due to hydrolysis of products (EGDN, MTN, PETN); and (c) the specific rate decreases as the reaction proceeds (DEGDN, TEGDN). Dinitrates fall into either the first or the second group, depending often on the distance between the $-ONO_2$ groups; long chain molecules, such as butane 1,4-diol and pentane 1,5-diol dinitrates, belong to class (a). The reason for the decrease in k shown by members of class (c) is not known, although one possibility is that the samples were not pure but contained small amounts of a faster reacting nitrate. Similar behaviour was found with TEGDN.

The specific rates of Tables 1 and 2 have been extrapolated to zero time to give the values of k_1 listed in Table 4. Stability of nitrates increases as the chain length increases, and is further enhanced by the replacement of an α -hydrogen by a methyl group:

CH_3ONO_2	$CH_3CH_2ONO_2$	$CH_3CH_2CH_2ONO_2$
112	4.4	2.9
CH_3CHONO_2 CH ₃	$C_6H_{13}CHONO_2$ CH ₃	
0.65	0.7	

Further substitution on the α -carbon leads to the change in mechanism already discussed. Alkyl substitution in the β position (as in going from ethyl to *n*-propyl to *iso*-butyl nitrate) has a smaller effect, but still tends to increase stability. This is not the case with β substitution by the groups $-OH$, $-ONO_2$, or $-NO_2$: EGDN reacts six hundred times more rapidly than ethyl nitrate, and the stability of EGDN at 30°C is no greater than that of EGDN. An interesting relationship also exists between the nitrates of ethanol, 2-nitroethanol, metriol, and 2-hydroxymethyl 2-nitropropane 1,3-diol (MIBG). The decomposition of 2-nitroethyl nitrate is best followed spectrophotometrically even though the reaction is only moderately fast. This is because of nitro- \rightleftharpoons ac-nitro tautomerism: the primary nitro group imparts weakly acidic properties to the molecule, enabling it to react (although slowly) reversibly with hydroxide ion to form a salt.



Titration of the reaction mixture with acid converts this salt into the aci form (more acidic than the parent nitro compound) which undergoes a slow rearrangement. This aci \rightarrow nitro change leads to a continual decrease in

/acidity,

acidity, with a concomitant change in pH and titr. value. The apparent hydroxyl ion concentration of the solution at any time is not, therefore, a measure of the extent of hydrolysis. Since the rate of salt formation is considerably faster than the rate of ester hydrolysis, the decomposition of $\text{O}_2\text{N} = \text{CHCH}_2\text{ONO}_2$ to $\text{O}_2\text{N} = \text{CHCH}_2\text{OH}$ can be followed spectrophotometrically as long as the hydroxide ion concentration is kept constant, a condition satisfied by pseudo first order kinetics. While the rate of ethyl nitrate hydrolysis at 30°C is not known, a reasonable value for the specific rate can be deduced from reported activation energies (4) for related alkyl nitrates as $0.22 \times 10^{-3} \text{ l.}^{-1} \text{ s.}^{-1}$

$\text{CH}_3\text{CH}_2\text{ONO}_2$	$\text{O}_2\text{NCH}_2\text{CH}_2\text{ONO}_2$ (as $\text{O}_2\text{N} = \text{CHCH}_2\text{ONO}_2$)
0.22	1050
CH_2ONO_2	CH_2ONO_2
$\text{CH}_3 - \text{C} - \text{CH}_2\text{ONO}_2$	$\text{O}_2\text{N} - \text{C} - \text{CH}_2\text{ONO}_2$
CH_2ONO_2	CH_2ONO_2
69	128,000

Thus replacement of H- by $\text{O}_2\text{N}-$ increases the rate of decomposition by a factor of 4800, while a similar replacement of a CH_3- group increases the rate some 1800 times (there is, of course, no aci-nitro tautomerism possible in the case of NIBG compounds). This destabilization is not confined to alkyl nitro compounds: 4-nitrobenzyl nitrate is hydrolysed 9000 times faster than benzyl nitrate (10), and the hydrolysis of 2,4-dinitrobenzyl nitrate is complete within the time of mixing.

Rates of hydrolysis increase in the presence of additional nitrate groups; the effect is most marked when the substitution is on the β -carbon, particularly if this is also a terminal atom. Propane 1,2-diol dinitrate reacts 1500 times faster than the n-propyl ester, while butane 2,3-diol dinitrate reacts only 22 times faster than the secondary mononitrate, $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_3$. Comparison of n- and iso-propyl nitrates or of butane 1,3- and 2,3-diol dinitrates shows that a primary $-\text{ONO}_2$ group is less stable than a secondary, and this seems to hold generally unless the secondary nitrate is activated by two adjacent nitrate groups, for it has been found (11) that partial hydrolysis of nitroglycerine yields a mixture of glycerol 1,3- and 1,2-dinitrates with the 1,3 isomer predominating.

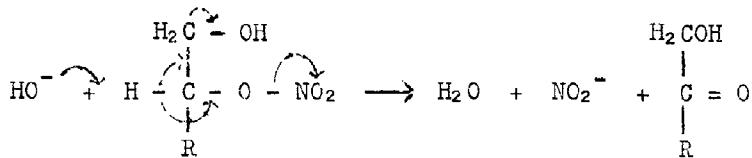
/Glycerol

Glycerol 1,3-dinitrate, with the secondary nitrate group missing, reacts five times slower than nitroglycerine, and the 1- and 2-mononitrates react slower still:

$\begin{array}{c} \text{CH}_2\text{ONO}_2 \\ \\ \text{CHONO}_2 \\ \\ \text{CH}_2\text{ONO}_2 \end{array}$	$\begin{array}{c} \text{CH}_2\text{ONO}_2 \\ \\ \text{CHOH} \\ \\ \text{CH}_2\text{ONO}_2 \end{array}$	$\begin{array}{c} \text{CH}_2\text{ONO}_2 \\ \\ \text{CHOH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHONO}_2 \\ \\ \text{CH}_2\text{OH} \end{array}$
0.24	0.045	0.022	0.009

although the decrease in hydrolysis rate on moving the nitrate group from the 1 to the 2 position is only half that found in the change from the 1 to the 2 position in propanol, with the increased instability resulting from the presence of the hydroxyl groups.

The stabilization-destabilization of an ester can be related to the inductive effect of the substituents. Electron release by a group decreases the rate of hydrolysis (methyl > ethyl > iso-propyl) because the large induced charge on the α -carbon hinders the approach of the attacking nucleophile (5). Electron attracting groups such as $-\text{OH}$, $-\text{NO}_2$, and $-\text{ONO}_2$ have the opposite effect. Both electromeric and inductive effects influence the carbonyl reaction (6), but the proportion (as opposed to the rate) of nitrite formation depends mainly on the electromeric effect and increases from methyl to iso-propyl. The interplay of the two effects becomes an important consideration in the reactions of polynitrates, where loss of the first group generates electron attracting centres such as $-\text{OH}$ or $-\text{CHO}$ and these in turn facilitate hydrogen ionization and the possibility of carbonyl elimination.

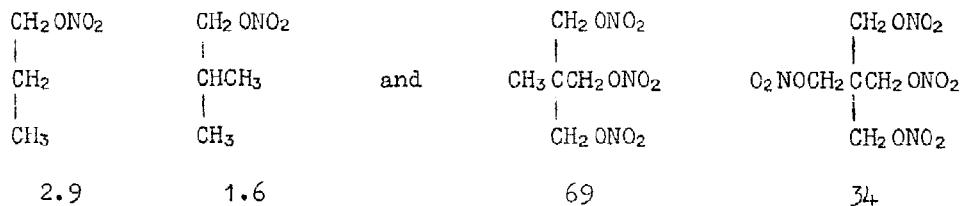


The closer the second nitrate group, the greater the effect, and typical results are shown in Table 5.

/4.4

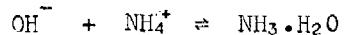
4.3 Steric Effects

Steric effects are more difficult to examine. Molecular models indicate that in the mononitrates a large area of the α -carbon is exposed to attack, so that electronic rather than steric effects must be invoked to account for the relatively slow rates encountered. This is the basis of the suggestion (5) that there is considerable repulsion between the approaching nucleophile and the negative charge field at the oxygen end of the nitrate dipole. It is clear, however, that as substitution of the β -carbon increases, the esters increase in stability.



4.4 Added Salts

It is known that solid ammonium perchlorate will accelerate the decomposition of nitrate esters. The results shown in Figure 2 indicate that ammonium perchlorate or nitrate dissolved in 90% aqueous alcohol, in the presence of hydroxide, has the opposite effect: the decomposition of the esters is inhibited. Similar concentrations of either sodium perchlorate or nitrate have no effect at all: in their absence the rate of hydrolysis of n-butyl nitrate is $2.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$; in their presence 2.9 and $3.1 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ respectively. Inhibition by ammonium salts results from the reduction of hydroxide ion concentration in the reaction mixture through combination with the ammonium ion:



/5.

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/GLOSSARY

GLOSSARY

1,3-BDN	Butane 1,3-diol dinitrate
2,3-BDN	Butane 2,3-diol dinitrate
1,4-BDN	Butane 1,4-diol dinitrate
DEGDN	Diethylene glycol dinitrate
EGDN	Ethylene glycol dinitrate
EGMN	Ethylene glycol mononitrate
1,3-GDN	Glycerol 1,3-dinitrate
1-GMN	Glycerol 1-mononitrate
2-GMN	Glycerol 2-mononitrate
MTN	Trimethylol ethane trinitrate
NG	Nitroglycerine
NIBG	2-Hydroxymethyl 2-nitropropane 1,3-diol
1,2-PDN	Propane 1,2-diol dinitrate
1,3-PDN	Propane 1,3-diol dinitrate
1,5-PDN	Pentane 1,5-diol dinitrate
PETN	Pentaerythritol tetranitrate
TEGDN	Triethylene glycol dinitrate
TEGMN	Triethylene glycol mononitrate

/TABLE 1

TABLE 1

Alkaline Hydrolysis of Nitrates in 90% (v/v) Ethanol

Nitrate Ester	Temp., °C	Time, s	[RONO ₂]	[NaOH]	$10^5 k_2$, M ⁻¹ s ⁻¹
methyl nitrate	60.0	0	0.0462	0.1032	
		15900	0.0082	0.0704	94
		20100	0.0061	0.0683	87
<u>n</u> -propyl nitrate	60.0	0	0.0336	0.1010	
		253800	0.0176	0.0850	2.75
		337500	0.0141	0.0815	2.88
		362500	0.0143	0.0817	2.62
		436500	0.0112	0.0786	2.86
		449100	0.0103	0.0777	3.03
<u>n</u> -butyl nitrate	60.0	0	0.0252	0.1132	
		336600	0.0087	0.0967	3.03
		360000	0.0080	0.0960	3.08
		522800	0.0056	0.0936	2.84
<u>n</u> -heptyl nitrate	60.0	0	0.0255	0.1030	
		81900	0.0205	0.0980	2.61
		325800	0.0125	0.0900	2.35
		433800	0.0085	0.0860	2.74
butane 2,3-diol dinitrate (2,3-BON)	30.0	0	0.0281	0.0905	
		154080	0.0191	0.0815	2.9
		181980	0.0181	0.0805	2.8
		241980	0.0156	0.0780	2.9
butane 1,4-diol dinitrate (1,4-BON)	60.0	0	0.0217	0.1065	
		6120	0.0198	0.1046	15.1
		7020	0.0192	0.1040	16.2
		15120	0.0167	0.1015	16.8
		20220	0.0157	0.1005	15.7

/pentane

Nitrate Ester	Temp., °C	Time, s	[R ₂ NO ₂]	[NaOH]	$10^5 k, \text{ s}^{-1}$
pentane 1,5-diol dinitrate (1,5-PDN)	60.0	0	0.0143	0.1070	
		15300	0.0117	0.1044	12.5
		27300	0.0099	0.1026	12.9
		33700	0.0069	0.0996	8.5
		90300	0.0043	0.0970	13.9
		108300	0.0039	0.0966	11.9
iso-butyl nitrate	60.0	0	0.1015	0.0309	
		10980	0.1010	0.0304	1.60
		61120	0.0980	0.0274	1.43
		166920	0.0930	0.0224	1.81
		253620	0.0910	0.0204	1.66
glycerol 1-mononitrate (1-GMN)	60.0	0	0.1175	0.0565	
		30	0.0730	0.0120	51000
	30.0	0	0.1410	0.0400	
		120	0.1010	0.0360	2170
		250	0.0925	0.0275	2180
		360	0.0890	0.0240	2060
		450	0.0835	0.0185	2170
		630	0.0785	0.0135	2200
glycerol 2-mononitrate (2-GMN)	60.0	0	0.0936	0.0236	
		31	0.0835	0.0135	20200
		105	0.0735	0.0035	22000
	30.0	0	0.1060	0.0330	
		90	0.1040	0.0310	900
		240	0.0995	0.0265	910
		390	0.0965	0.0235	900
		580	0.0910	0.0180	970

TABLE 2

TABLE 2
Alkaline Hydrolysis of Nitrates in 90% (v/v) Ethanol

Nitrate Ester	Temp., °C	Time, s	[RONO ₂]	[NaOH]	$10^5 k, \frac{M^{-1}}{s^{-1}}$
Ethylene glycol mononitrate (EGMN)	30.0	0	0.0291	0.1010	
		290	0.0256	0.0975	180
		600	0.0246	0.0965	147
		900	0.0216	0.0935	152
		1380	0.0191	0.0910	188
		6000	0.0111	0.0830	147
		8400	0.0061	0.0780	195
	60.0	0	0.0150	0.0950	
		20	0.0140	0.0940	2740
		135	0.0075	0.0875	5200
		220	0.0040	0.0840	6800
Ethylene glycol dinitrate (EGDN)	30.0	0	0.0268	0.1027	
		1140	0.0189	0.0948	308
		2040	0.0114	0.0873	447
		3000	0.0069	0.0828	501
	propane 1,2-diol dinitrate (1,2-PDN)	0	0.0260	0.1016	
		810	0.0248	0.1004	583
		1860	0.0320	0.0988	61.5
		3150	0.0194	0.0950	94.9
		5940	0.0132	0.0888	121
	60.0	0	0.0262	0.1020	
		405	0.0080	0.0838	3300
		615	0.0060	0.0764	2540

/propane

Nitrate Ester	Temp., °C	Time, s	[RONO ₂]	[NaOH]	$\cdot 10^5 k, \frac{M^{-1}}{s^{-1}}$
propane 1,3-diol dinitrate (1,3-PDN)	30.0	0	0.0348	0.1080	
		720	0.0333	0.1065	52.5
		1380	0.0318	0.1050	61.6
		1860	0.0308	0.1040	61.0
		2580	0.0293	0.1025	62.0
		5100	0.0258	0.0990	56.0
		6300	0.0238	0.0970	59.0
	60.0	0	0.0330	0.100	
		195	0.0260	0.0930	1270
		255	0.0235	0.0905	1390
		350	0.0220	0.0890	1230
butane 1,3-diol dinitrate (1,3-BDN)	30.0	0	0.0235	0.1035	
		77920	0.0140	0.0940	23.2
		104020	0.0110	0.0910	16.1
		184420	0.0095	0.0895	17.6
		251020	0.0050	0.0850	22.8
butane 2,3-diol dinitrate (2,3-BDN)	60.0	0	0.0281	0.0994	
		3540	0.0226	0.0939	63.3
		15720	0.0137	0.0850	50.0
Diethylene glycol dinitrate (DEGDN)	60.0	0	0.0253	0.1052	
		210	0.0240	0.1039	240
		450	0.0235	0.1034	157
		915	0.0230	0.1029	100
		1260	0.0219	0.1018	111
		2130	0.0217	0.1016	70
		15740	0.0135	0.0934	46.3

/Triethylene

Nitrate Ester	Temp., °C	Time, s	[RONO ₂]	[NaOH]	$10^5 k_2 \text{ s}^{-1}$
Triethylene glycol dinitrate (TEGDN)	60.0	0	0.0209	0.1068	
		1140	0.0169	0.1028	175
		1950	0.0153	0.1012	153
		3660	0.0155	0.1014	77
		4380	0.0151	0.1010	71
		6060	0.0145	0.1004	57
		10320	0.0139	0.0998	39
metriol trinitrate (MTN)	60.0	0	0.0189	0.0935	
		400	0.0184	0.0930	69.5
		1660	0.0169	0.0915	71
		4460	0.0129	0.0875	101
		6150	0.0099	0.0845	119
Pentaerythritol tetranitrate (PETN)	60.0	0	0.0064	0.0960	
		90	0.0049	0.0915	2740
		225	0.0009	0.0875	7600
glycerol 1,3-dinitrate (1,3-GDN)	60.0	0	0.1030	0.0198	
		40	0.0850	0.0018	66200
	30.0	0	0.1090	0.0255	
		90	0.1000	0.0165	4650
		160	0.0950	0.0115	4900
		240	0.0910	0.0075	5200
		330	0.0845	0.0010	10800

/TABLE 3

TABLE 3

Rate Constants Determined Spectrophotometrically
(90% v/v ethanol; 30.0°C)

Nitrate Ester	[Nitrate]	[Hydroxide]	$k, \text{M}^{-1} \text{s}^{-1}$
NG	0.0021	0.0518	0.24
NIBG trinitrate	0.0005	0.0071	1.28
PETN	0.0051	0.1172	3.48×10^{-4}
2-nitroethyl nitrate	0.0009	0.0118	1.05×10^{-2}

TABLE 4

TABLE 4
Summary of Initial Specific Rates
 $(\text{M}^{-1} \text{s}^{-1})$

Nitrate Ester	$10^5 k_i$		Nitrate Ester	$10^5 k_i$	
	30°C	60°C		30°C	60°C
methyl nitrate		112	TEGDN		340
ethyl nitrate (Ref. 4)		4.4	1,2-PDN	54	4650
n-propyl nitrate (Ref. 4)		2.9	1,3-BDN	20	
n-butyl nitrate		2.9	2,3-BDN	2.9	66
n-heptyl nitrate		2.6	MTN	69	
iso-propyl nitrate (Ref. 4)		0.65	NG	24000	
iso-butyl nitrate		1.6	1,3-GDN	4500	66200
tert-butyl nitrate (Ref. 4)	24		1-GMN	2150	51000
EGMN	168	2700	2-GMN	920	20500
EGDN	160		NIBG	128000	
1,3-PDN	58.7	1300	PETN	34	2700
1,4-BDN		16.0	2-nitro- ethyl nitrate	1050	
1,5-PDN		12.5			
DEGDN		340	2-octyl nitrate (Ref. 2)		0.7

/TABLE 5

TABLE 5
Nitrite Formation in Alkaline Hydrolysis

Nitrate Ester	$\text{NO}_2^- / k_{\text{total}}$	Reference
methyl nitrate	-	
ethyl nitrate	0.048	4
<u>n</u> -propyl nitrate	0.031	
<u>n</u> -butyl nitrate	0.0024	
<u>iso</u> -propyl nitrate	0.136	4
<u>tert</u> -butyl nitrate	0.54	4
1,2-PDN	0.173	
TEGDN	0.065	

/KEY

KEY TO FIGURES

Figure 1 The reaction vessel of Teflon and steel.

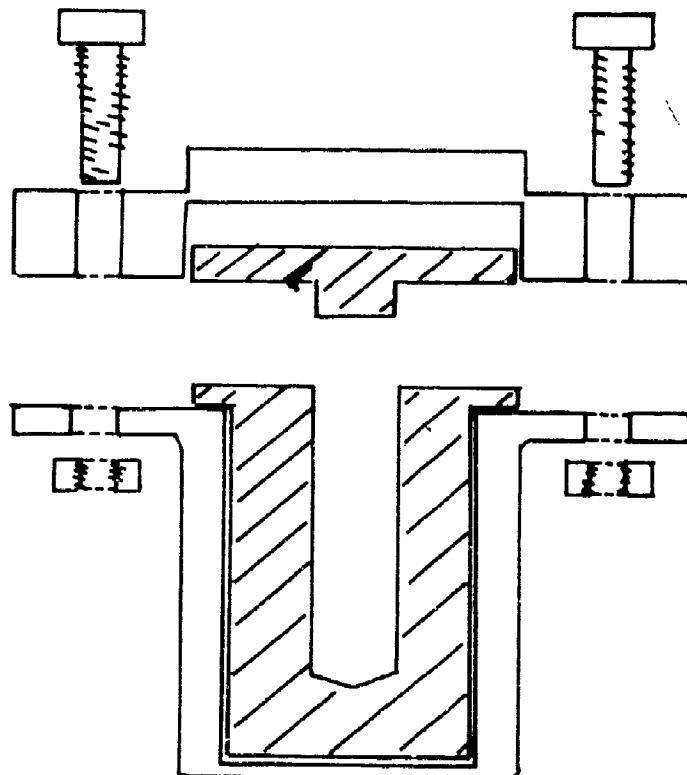
Figure 2 The rate of hydrolysis of n-butyl nitrate in solutions containing hydroxide, perchlorate and nitrate ions.

a = amount of hydroxide

b = amount of ester

S.No. 23/68/RR/GJ

ERDE 4/R/68

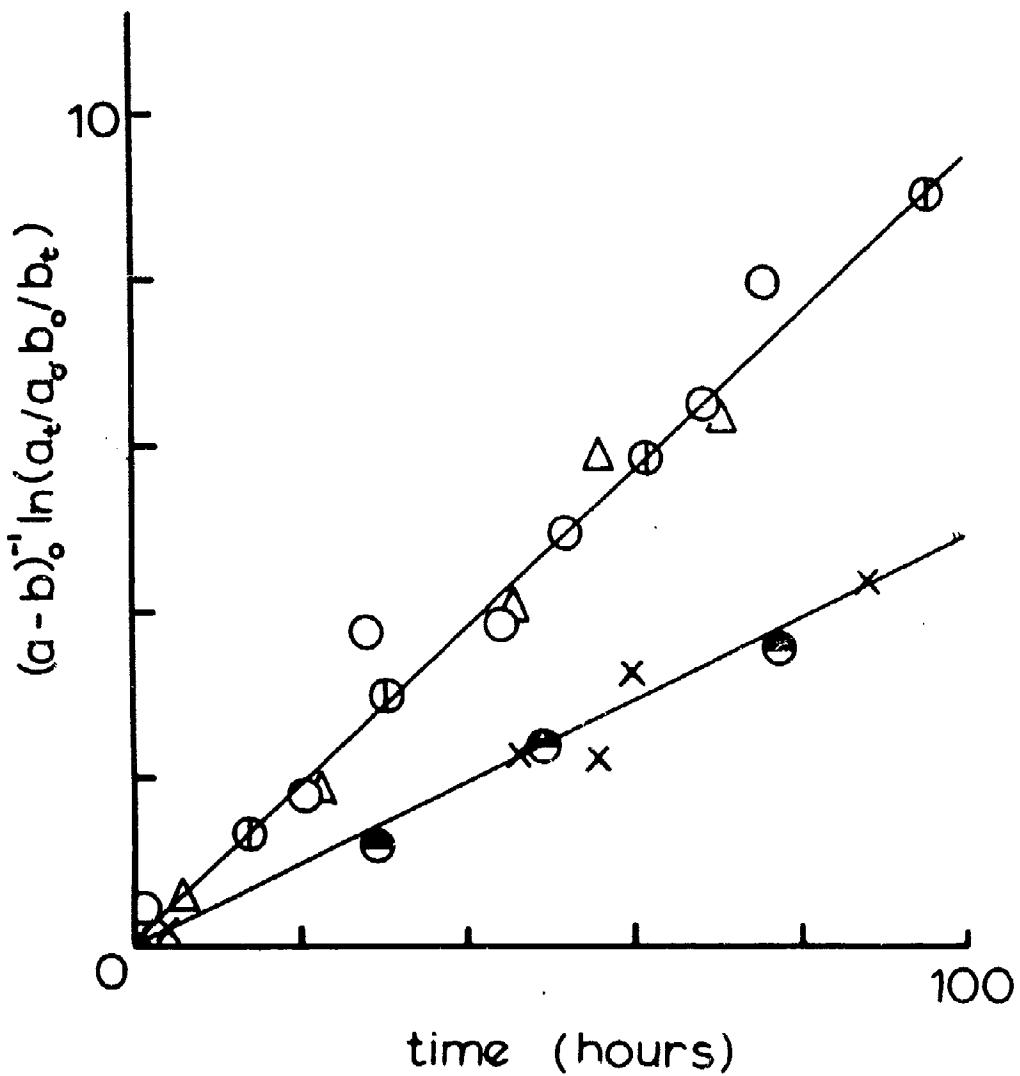


□ steel

▨ Teflon

Figure 1

ERDE 4/R/68



- no added salt
- △ N/10 NaClO₄
- N/10 NaNO₃
- x N/10 NH₄ClO₄
- N/10 NH₄NO₃

Figure 2